

Full Paper

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**A Study of Bisazido(dimethylaminopropyl)gallium as a Precursor for the OMVPE of Gallium Nitride Thin Films in a Cold-Wall Reactor System under Reduced Pressure\*\***

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By Anjana Devi, Wolfram Rogge, Andreas Wohlfart, Frank Hipler, Hans W. Becker, and Roland A. Fischer\*

The use of alternative nitrogen sources for growing GaN materials by organometallic vapor phase epitaxy (OMVPE) is being continuously investigated in the hope of achieving device-quality films under moderate conditions, in comparison to conventional methods. Employing the single molecule precursor  $(N_3)_2Ga[(CH_2)_3NMe_2]$ , and using a cold-wall CVD reactor, epitaxial films of GaN, transparent in appearance and stoichiometric in composition, were deposited on *c*-plane sapphire, in the absence of ammonia, above 1073 K, under low pressures (between 0.080 and 100.0 mbar). Dense, amorphous, and very smooth films were grown at temperatures as low as 773 K. The influence of substrate temperature, reactor pressure, and the effect of small quantities of additional ammonia, on the growth rate and the film properties, were studied in some detail. The films were characterized by high-resolution X-ray diffraction (XRD) (e.g., full width at half maximum (FWHM) of the 0002 GaN rocking curve of 130 arcsec), X-ray reflectometry, scanning electron microscopy (SEM), atomic force microscopy (AFM) (root mean square roughness of 1.9 nm), X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), Rutherford backscattering (RBS) (Ga/N = 1:1  $\pm$  0.05), and photoluminescence (PL) measurements (band edge luminescence at 3.45 eV and FWHM of 0.22 eV at 300 K).

Keywords: Azides, Gallium nitride, OMVPE, Single-molecule precursors, Thin films

**1. Introduction**

The interest in developing new approaches to growing the group 13 nitrides AlN, GaN, and InN has been motivated by the fact that these materials have found practical applications in optoelectronic devices such as green/blue light-emitting (laser) diodes.<sup>[1-3]</sup> The industrial production of nitride-based devices is accomplished by conventional thermally activated OMVPE, which employs the co-pyrolysis of metal alkyls such as GaMe<sub>3</sub> with a large excess of ammonia (>1000) at high temperatures (~1373 K).<sup>[4,5]</sup> Efforts have been made to replace the inefficient N-source ammonia (which requires very high temperatures, above 973 K, to be activated) with alternative nitrogen precursors exhibiting lower thermal stability. Recently, there has been growing interest in GaAsN alloys, typically containing a few atomic percent of nitrogen. Thermally labile nitrogen precursors have potential in the OMVPE of these alloys, in addition to the wider bandgap group 13 nitrides.<sup>[5]</sup> Indeed,

the growth at lower V/III ratios and under milder growth conditions has been achieved with hydrazine (N<sub>2</sub>H<sub>4</sub>), 1-1-dimethyl hydrazine (Me<sub>2</sub>NNH<sub>2</sub>), phenyl hydrazine (PhNH-NH<sub>2</sub>), *tert*-butyl hydrazine (t-BuNH-NH<sub>2</sub>), and hydrazoic acid (HN<sub>3</sub>).<sup>[6-10]</sup> However, these N-sources are likely to be of limited technical use due to their very toxic and explosive nature. Alkyl amines (RNH<sub>2</sub>, R = 'Bu, 'Pr) have also been studied, but carbon incorporation is a severe problem with these precursors.<sup>[11,12]</sup> One approach to replacing the pyrophoric alkyls and avoiding very large amounts of toxic ammonia, as well as lowering the deposition temperatures, is to develop single-molecule precursors (SMPs) containing both the metal and nitrogen atoms. The general idea is that SMPs may provide a more efficient delivery of the growth species to the surface where, ideally, they should directly and cleanly convert to the desired material. Because organometallic amide species such as Me<sub>n</sub>-Ga<sub>6</sub>(NH<sub>x</sub>)<sub>n</sub> are formed as intermediates on mixing GaMe<sub>3</sub> and ammonia in the gas phase, group III metal amido compounds such as [R<sub>2</sub>GaNH<sub>2</sub>]<sub>3</sub> and [Ga(NR<sub>2</sub>)<sub>3</sub>]<sub>2</sub> (R = Et, Me) are likely candidates as SMPs for GaN, and have been studied as sources for the growth of group 13 nitrides with, however, limited success in terms of the achieved film properties.<sup>[13-16]</sup>

In exploring other ways of introducing a nitrogen source into a SMP for GaN, some researchers took advantage of the azide moiety by incorporating it into a Ga precursor molecule such as [R<sub>2</sub>GaN<sub>3</sub>]<sub>x</sub> (R = Cl, H, Et, Me).<sup>[17-20]</sup> The azide group combines a pre-formed strong Ga-N bond with a simultaneously reduced number of undesired Ga-C and

[\*] Prof. R. A. Fischer, Dr. A. Devi, Dr. W. Rogge, A. Wohlfart, F. Hipler, Dr. H. W. Becker  
Lehrstuhl für Anorganische Chemie II  
Ruhr Universität Bochum  
Universitätsstr. 150, D-44780 Bochum (Germany)  
E-mail: rfischer@aci.ruhr-uni-bochum.de

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N–C bonds, hence minimizing the probability of carbon incorporation into the nitride material during growth. The fragmentation of the azide units into the inactive leaving group, dinitrogen, and a reactive nitrene intermediate, is a well-established decomposition pathway of covalent azides.<sup>[21]</sup> Thus using group 13 metal azide-based precursors, it is likely that MN species may be formed in the boundary layer, or directly at the substrate surface. In the presence of ammonia, the metal azide unit can probably undergo ammonolysis similar to the alkyl amide type of precursors, but producing  $\text{HN}_3$  instead of alkyl amines. Hydrazoic acid itself can act as an efficient source of nitrogen and, in the case of the ammonolysis of metal azides in the gas phase,  $\text{HN}_3$  would be produced in situ only in the reactor close to the substrate surface (thus circumventing the intrinsic problems associated with the use of explosive  $\text{HN}_3$  as a separate source for nitrogen). A rather extreme example of the azide concept is the use of  $[\text{H}_2\text{GaN}_3]_3$  as a hydrocarbon-free GaN precursor.<sup>[22]</sup> However, this compound is very air-sensitive and explosive. Taking these factors into consideration, the problem is to derive nitrogen-rich precursors that can be handled safely, and that are fully compatible with conventionally used metal–organic chemical vapor deposition (MOCVD) equipment, and the growth process for the nitrides. We have concentrated our research activity on developing intramolecularly Lewis base-stabilized organometallic azide compounds of the type  $(\text{N}_3)_a\text{M}[(\text{CH}_2)_3\text{NMe}_2]_{3-a}$  ( $\text{M} = \text{Al}, \text{Ga}, \text{In}$  and  $a = 1, 2$ ). These compounds were found to be sufficiently volatile due to their monomeric, or only very weakly associated, structure in the solid state. In addition, they proved to be non-pyrophoric, non-explosive, and, in the case of the In compound, even air stable. Their general suitability for the deposition the nitride materials has been demonstrated by very simple hot-wall CVD in vacuo.<sup>[23–26]</sup> The aim of this study is to give a comprehensive account of the application of the precursor bisazido dimethylaminopropyl gallium (BAZIGA) under more realistic conditions (using a cold-wall reactor under reduced pressure).

## 2. Results and Discussion

### 2.1. Precursor Characterization

Our goal was to obtain very pure SMPs because the growth of device-quality films will only be achieved with high-purity precursors. The purity of the precursor depends on both the purity and integrity of the starting materials, and on the synthesis route itself. It is therefore essential that the precursors can be synthesized in a pure form by a reproducible process, and can be fully characterized for organic and metallic impurities. The organometallic precursor BAZIGA was obtained in the form of colorless needles at or below room temperature after repeated purification by short-path flask-to-flask distillation at 423 K using a tur-

bomolecular pump ( $10^{-5}$  mbar, dynamic vacuum). Details of the synthesis, characterization, and the crystal structure of BAZIGA have been published elsewhere.<sup>[27]</sup> The compound is non-pyrophoric as well as non-explosive (sudden heating, mechanical shock, laser irradiation of a bulk sample using a 308 nm excimer laser). The volatilization and the thermal stability of the precursor were investigated by thermogravimetric and differential thermal analysis (TG/DTA). Figure 1 shows the TG/DTA plot of BAZIGA under ambient pressure. From the TG curve it can be seen

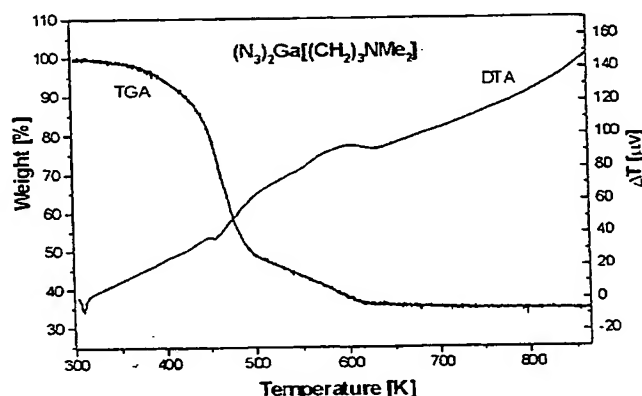


Fig. 1. TG/DTA of  $(\text{N}_3)_2\text{Ga}[(\text{CH}_2)_3\text{NMe}_2]$  under ambient pressure (argon flow rate =  $100 \text{ mL min}^{-1}$  and heating rate  $5 \text{ K min}^{-1}$ ).

that there is monotonic weight loss (volatilization) up to a temperature of about 473 K, followed by a step at 493 K (broad exothermic DTA peak), which can be attributed to the onset of decomposition of BAZIGA, and above 673 K a residue of about 35 % is left in the crucible. From the DTA curve an endothermic peak at 308 K, which corresponds to the melting point of BAZIGA, is observed. The precursor is stable between 353 and 373 K, the normal operating temperature range in a typical CVD run. The vapor pressure of BAZIGA between 300 K (2.5 mPa) and 433 K (16 Pa) was measured using standard methods and, employing a Netzsch VP433 vapor pressure balance, by the condensation and impulse method. The vapor pressure can be calculated using Equation 1.

$$\ln[p(T)] = 23.7 - 8840/T [\text{Pa}] \quad (1)$$

### 2.2. Deposition Characteristics

A schematic diagram of the low-pressure, horizontal, cold-wall reactor is shown in Figure 2. Initially, the intention was to grow GaN thin films on c-plane sapphire using BAZIGA and an inert carrier gas ( $\text{N}_2$ ) without the use of any additional nitrogen source such as ammonia. This was successfully achieved and it was found that amorphous GaN formed at temperatures lower than 973 K. No buffer layer was grown prior to film deposition, but the substrates were subjected to nitridation under the influence of ammo-

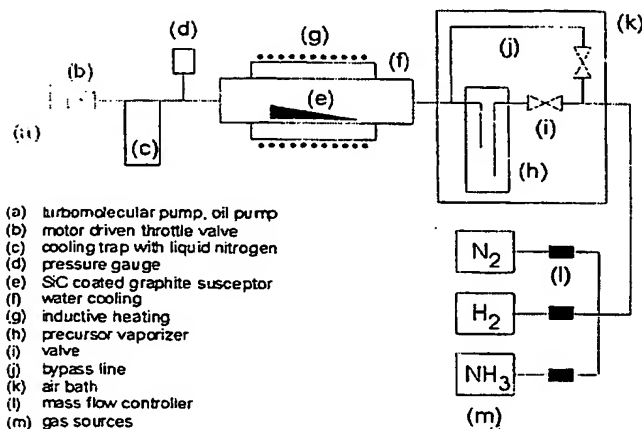


Fig. 2. Schematic diagram of the cold-wall CVD reactor

nia flow (40 sccm) for 30 min at 1223 K. When the substrate temperature was increased above 973 K, crystalline GaN was formed, and at temperatures as low as 1073 K epitaxial films were obtained. Film growth experiments, which were conducted using substrate temperatures in the range 773–1323 K, yielded transparent films of GaN. With the reactor pressure maintained at 0.080 mbar, a vaporizer temperature of 363 K, a substrate temperature of 1073 K, and a typical growth run duration of 45 min, growth rates of the order of  $4500 \text{ nm h}^{-1}$  were measured. With the reactor pressure maintained at 8.000 mbar, a vaporizer temperature of 363 K, and no ammonia used for the deposition of GaN, the dependence of growth rate on substrate temperature is shown in Figure 3a. In the temperature range 870–1000 K, the growth rate increases with temperature with an apparent activation energy  $E_a$  of  $151 \pm 5 \text{ kJ mol}^{-1}$ , while at higher temperatures (1025–1173 K), the growth rate levels off. The maximum growth rate of  $2500 \text{ nm h}^{-1}$  was obtained at a substrate temperature of 1173 K under the given set of

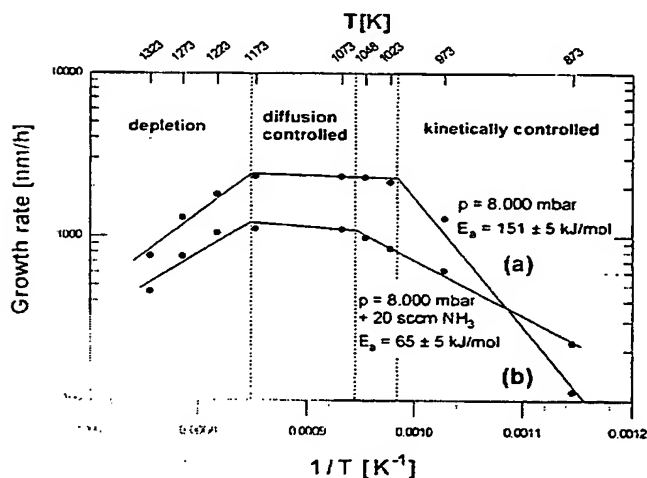


Fig. 3. Growth rate of GaN films grown on *c*-plane  $\text{Al}_2\text{O}_3$  as a function of temperature. (a) growth rate of GaN at pressure 8.000 mbar without ammonia. (b) growth rate of GaN at pressure 8.000 mbar and ammonia flow rate 20 sccm (vaporizer temperature was maintained at 363 K for all depositions).

conditions. At even higher temperatures (above 1173 K) the growth rate decreases. When similar studies were conducted under lower pressure (0.080 mbar), the growth rates were higher (roughly double) and the maximum growth rate of  $4500 \text{ nm h}^{-1}$  was obtained at 1073 K. Moreover, the apparent energy of activation showed a pressure dependence, decreasing to  $85 \pm 5 \text{ kJ mol}^{-1}$  for GaN films grown under lower pressure (0.080 mbar).

### 2.3. Effect of Ammonia on the Growth Rate of GaN

Although no additional source of nitrogen (such as ammonia) was necessary to grow epitaxial and stoichiometric GaN films using BAZIGA, we were interested in investigating the effect of ammonia on the growth process. Keeping the total pressure constant at 8.000 mbar and the vaporizer temperature at 363 K, but varying the ammonia gas flow rate, similar experiments to those described above were carried out. Figure 3b shows the dependence of growth rate on substrate temperature. The apparent activation energy was lowered by more than half ( $65 \pm 5 \text{ kJ mol}^{-1}$ ), which clearly shows that ammonia plays an active role in the deposition kinetics. The growth rate was also reduced, the highest growth rate obtained being of the order of  $1000 \text{ nm h}^{-1}$ . As in the previous experiment, the growth rate dropped off at higher temperatures. Another important observation was that the film quality, in terms of crystallinity, was poorer (as will be discussed in the following sections) compared to those films grown in the absence of ammonia. Studies are underway to investigate the mechanisms involved during the growth process, with and without ammonia, by probing the species from the gas phase that are generated close to the substrate surface during the deposition of GaN, as determined by the molecular beam sampling method, using quadrupole mass spectrometry (MS) (electron impact ionization), as well as resonance-enhanced multiphoton ionization time-of-flight (REMPI/TOF) MS. Preliminary results on this issue have recently been communicated.<sup>[28]</sup>

### 2.4. GaN Film Properties

The procedure for the nitridation of the bare sapphire substrate was similar to that reported in the literature.<sup>[29]</sup> An amorphous, low-temperature (773 K) film of GaN, grown on a previously nitridated sapphire substrate without ammonia, with the reactor pressure maintained at 8.000 mbar, and a vaporizer temperature of 363 K, was characterized by X-ray reflectometry (Fig. 4). The data obtained can be fitted on the assumption that a multilayer structure involving an AlN interface of thickness 0.5 nm is present. The SEM investigation of this film revealed a microstructure consisting of small grains that are well connected. The nitridation of the bare sapphire substrate with  $\text{NH}_3$  at 1223 K (30 min) yields a 0.5 nm thick AlN layer, as

confirmed by X-ray reflectometry and XPS measurements. As verified by reflectometry, this AlN interface is absent in the case of the low-temperature growth of GaN films on non-nitridated substrates. The density of these low temperature-grown GaN layers was found to be significantly lower ( $4.42 \text{ g cm}^{-3}$ ) than crystalline bulk  $\alpha$ -GaN ( $6.1 \text{ g cm}^{-3}$ ) and this could be caused by several factors, including residual hydrocarbon fragments and other structural defects formed during growth. As a result of the rough surface of the film, high-temperature thin films could not be characterized by reflectometry.

XRD of GaN films confirmed that they were crystalline above 973 K. At temperatures below 973 K, the XRD patterns showed broad reflections with lower intensity, indicating that the films were either amorphous or partially crystalline. Epitaxial films were obtained at temperatures as low as 1073 K. The best crystalline quality films were obtained when deposited at 1173 K under 8.000 mbar reactor pressure, with a vaporizer temperature of 363 K, on nitridated substrates. Further increases in temperature did not increase the crystalline quality of the films. Figure 5a shows the XRD pattern of a GaN film grown on *c*-plane  $\text{Al}_2\text{O}_3$  at 1023 K under 8.000 mbar reactor pressure, with a vaporizer temperature of 363 K, and without ammonia. The film is seen to be polycrystalline with the 0002 reflection predominant, indicating the preferred orientation, with the [0001] direction of the GaN parallel to the [0001] direction of the underlying sapphire substrate. Figure 5b shows the 0002 X-ray rocking curve analysis of an epitaxial GaN film grown on *c*-plane  $\text{Al}_2\text{O}_3$  at 1173 K, with a reactor pressure of 8.000 mbar, a vaporizer temperature of 363 K, without ammonia. The FWHM obtained was 130 arcsec ( $0.036^\circ$ ). This is, to our knowledge, the best ever reported value for the epitaxial GaN films obtained from SMPs without any additional source of nitrogen. The growth of GaN from  $(\text{CH}_3)_3\text{Ga}$  and  $\text{NH}_3$ , at 1353 K, from independent sources on specifically pre-treated sapphire substrates (nitridated layers), according to the classical process, allows narrower rocking curves down to a minimum FWHM of 40 arcsec.<sup>[30]</sup> On the other hand, the FWHM of the epitaxial GaN films obtained using BAZIGA, with additional ammonia (2–20 sccm), under similar CVD process conditions, were not only higher, but were observed to increase with increasing ammonia flow (Fig. 5c). It is known that ammonia can be beneficial in achieving epitaxial growth when SMPs such as  $[\text{Et}_2\text{Ga}(\text{N}_3)_3]$  are used.<sup>[19]</sup> The authors attributed this effect to a lack of surface mobility of the oligomeric precursor fragments in the absence of ammonia. In our case, the fragmentation of the precursor BAZIGA is likely to produce smaller fragments, which may have sufficient surface mobility. An increasing concentration of ammonia caused an observable decrease of crys-

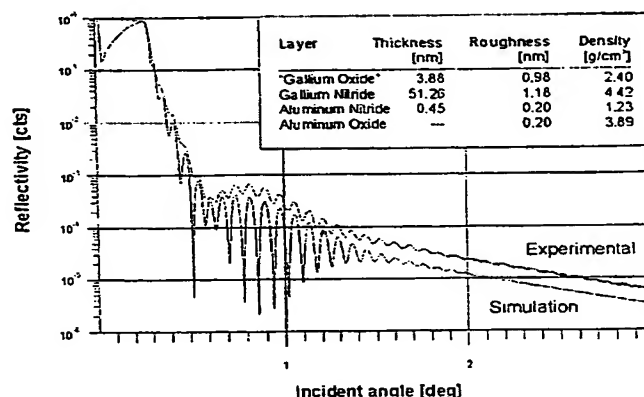


Fig. 4. X-ray reflectometry studies on a GaN film grown at low temperature (773 K) deposited from BAZIGA on *c*-plane  $\text{Al}_2\text{O}_3$ , without ammonia under 8.000 mbar reactor pressure, and with a vaporizer temperature of 363 K.

tallographic orientation of the material. However, it was found that the presence of ammonia does not change the gas-phase chemistry.<sup>[28]</sup> The partial pressure of BAZIGA in the reactor is reduced due to the constant reactor pressure (all other process parameters are kept constant and ammonia flow is the only variable). Thus it seems that ammonia plays an important role in terms of the chemistry on the surface, as is also indicated by the lowering of the apparent activation energy. The effect of ammonia on the crystal quality of GaN was the subject of further study.

It was found that the crystalline quality of the films was also strongly dependent on the deposition pressure. Narrow rocking curves were obtained at a reactor pressure of 8.000 mbar. Upon increasing the total pressure from

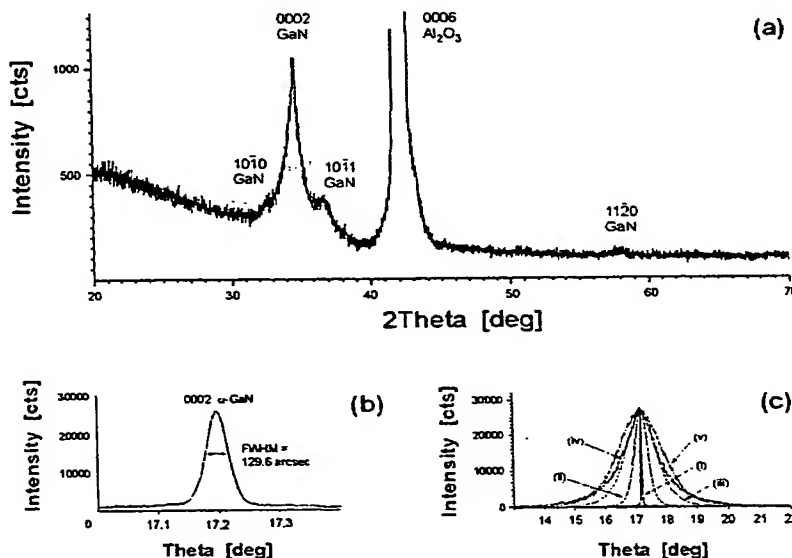


Fig. 5. XRD pattern of GaN films grown on *c*-plane  $\text{Al}_2\text{O}_3$ . a) Polycrystalline GaN film grown at 1023 K without ammonia. b) Rocking curve of an epitaxial GaN film grown at 1173 K without ammonia. c) Rocking curves of epitaxial GaN films grown at 1173 K as a function of ammonia flow: i) 0 sccm, ii) 5 sccm, iii) 10 sccm, iv) 15 sccm, v) 20 sccm. (All films were grown under a reactor pressure of 8.000 mbar and at a vaporizer temperature of 363 K.)

0.080 mbar to 10.0 mbar, the ratio between the signal intensity of the GaN 0002 reflection and the substrate peak of the films deposited at 1173 K improved dramatically (by a factor of 100). Further investigation of the crystalline quality of the GaN films was carried out by pole figure measurements and reciprocal space mappings, to characterize more precisely the structural relation of the layers grown relative to the substrate. Figure 6a shows the 2D plot of the XRD reciprocal space mapping for epitaxial

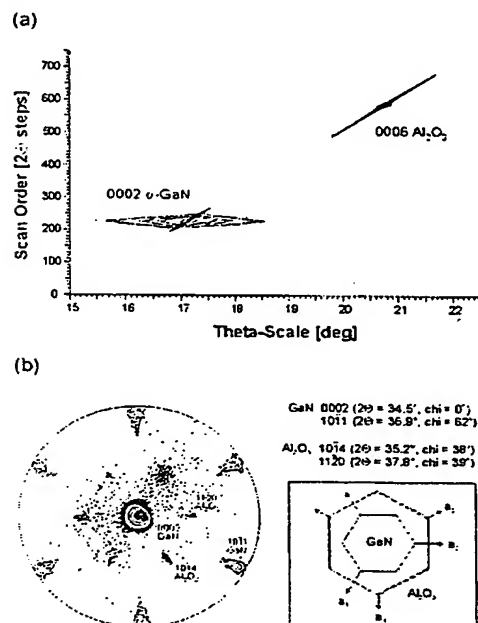


Fig. 6. a) 2D-plot of the XRD reciprocal space maps for epitaxial GaN film grown at 1173 K on c-plane Al<sub>2</sub>O<sub>3</sub>. b) Pole figure measurements on a GaN film grown at 1173 K on c-plane Al<sub>2</sub>O<sub>3</sub> (both films deposited from BAZIGA, without ammonia, under 8.000 mbar reactor pressure, vaporizer temperature maintained at 363 K). To the right hand side of Figure 6b is an illustration of the orientation of α-GaN film relative to the sapphire substrate (30°).

GaN layers grown at 1173 K, without ammonia, under 8.000 mbar reactor pressure, and with a vaporizer temperature of 363 K. The vertical and horizontal axes correspond to 2θ- and ω-scans, respectively (2θ values in steps of 0.02°). On the basis of this plot, a columnar growth of α-GaN in the [0001] direction has been determined and compared with a commercially grown α-GaN film, which showed a similar feature. To determine the orientation and epitaxial relationships of α-GaN to the c-plane sapphire substrate, the pole figure measurement of a α-GaN film was carried out. This was set up with fixed values of 2θ = 34.5° and ω = 17.25° to collect the X-rays diffracted (ψ = 0–65°, φ = 0–360°). The 2D plot (Fig. 6b) shows the reflections from GaN 0002 and 1011, and from the Al<sub>2</sub>O<sub>3</sub> substrate 1014 and 1120, at different ψ and φ angles. The orientation of the sapphire substrate is illustrated by three spots of 1014 and 1120 reflections, and the orientation of α-GaN is illustrated by six 1011 reflections. From the arrangement of these reflections, it is clear that the in-plane

orientation of α-GaN films deposited on c-plane sapphire substrate is 30° (as shown in Fig. 6b), a well recognized value.<sup>[31]</sup> The measurements and analysis of 2θ–θ scans, reciprocal space mappings, and pole figure measurements confirmed the hexagonal symmetry of the GaN layers deposited from BAZIGA.

From the detailed XRD analyses we have found that the crystalline quality of the GaN films deposited were improved at higher pressures (above 10.0 mbar), which can be attributed to the lower growth rate. At lower pressures (0.080 mbar), the growth rates were higher (lower *E<sub>a</sub>*), resulting in thicker films of lower crystalline quality, perhaps due to the formation of structural defects and the incorporation of some precursor fragments. As a result, the intensity of the reflections from α-GaN (as observed by XRD analyses) is lower.

## 2.5. Film Composition

The composition of the films was routinely checked by RBS spectroscopy, including nitrogen, carbon, and oxygen signals to determine the Ga–N stoichiometry and levels of impurity. The RBS analyses revealed stoichiometric GaN in a “chemical sense” that is 1:1 (±0.05) with material free of oxygen. In addition, channeling effects were observed during the RBS measurements for different angles, indicating the crystalline structure of the films. Electron probe microanalysis (EPMA) revealed the Ga to N ratio as 1:1 (±0.02). Although techniques such as RBS and EPMA were used to determine the film stoichiometry, they are not sufficiently sensitive to detect small nitrogen deficiencies in the film. Further investigation of the composition (with reference to defects and N-deficiencies), e.g., Hall measurements, electron mobility, and dopant levels, is underway. The films were also characterized by XPS and AES, and Figure 7a shows the XPS spectrum of a GaN film grown at 973 K, without ammonia, under 8.000 mbar reactor pressure, at a vaporizer temperature of 363 K. Figure 7b shows the XPS spectrum of a GaN film grown at 1173 K from BAZIGA, using ammonia, under 8.000 mbar reactor pressure, at a vaporizer temperature of 363 K. The GaN films were subjected to sputter-cleaning with an Ar ion beam for 3 min (sputtering rate of 3 nm min<sup>−1</sup>) to remove any surface contamination. Films grown without using ammonia contained small traces of carbon (Fig. 7a). This can be accounted for by the incomplete fragmentation of BAZIGA and loss of by-products (unsaturated alkyl amines), leading to carbon incorporation. On the other hand, carbon was absent (as shown in Fig. 7b) from the film grown at 1173 K, with 20 sccm NH<sub>3</sub>, under 8.000 mbar reactor pressure, and the vaporizer temperature maintained at 363 K. It was found that the presence of ammonia during deposition prevented the incorporation of carbon into the films. It is interesting to note that very small amounts of ammonia (2–5 sccm) were needed to grow carbon-free GaN films.

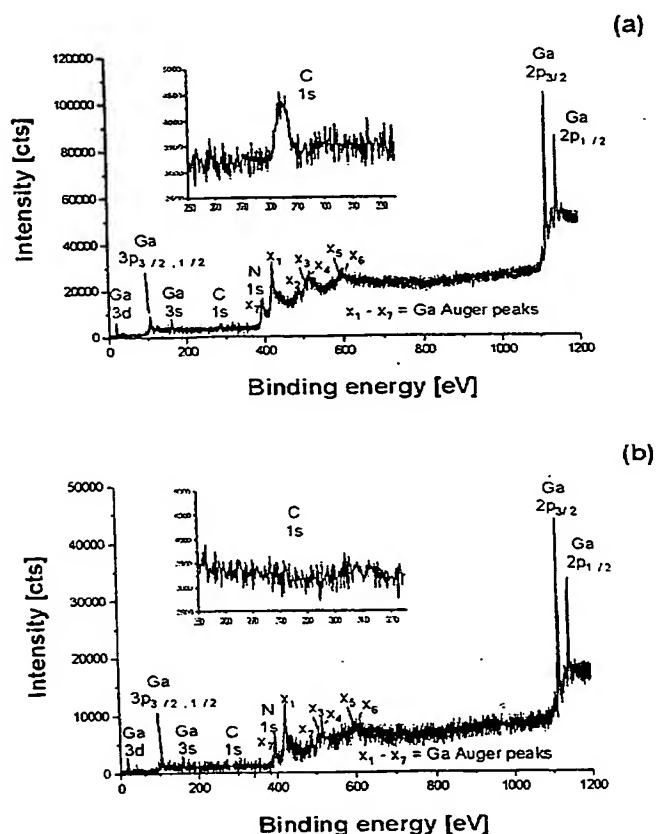


Fig. 7. XPS data of GaN films grown from BAZIGA on *c*-plane  $\text{Al}_2\text{O}_3$  at 1173 K: a) without ammonia. b) with ammonia (20 sccm). During the depositions, the reactor pressure was maintained at 8.000 mbar, and the vaporizer temperature at 363 K.

## 2.6. Film and Surface Morphology, Nucleation, and Buffer Layers

The surface morphology of the films was probed by AFM, and it can be seen from Figure 8a that some pyramidal-type features were observed for an amorphous GaN film grown at 773 K with ammonia (20 sccm). The substrate ( $1 \times 1 \text{ cm}^2$ ) was completely coated with GaN, and a surface roughness of  $\sim 2.2 \text{ nm}$  (rms) was measured. The rms surface roughness of a low-temperature GaN film deposited without ammonia at 773 K was slightly lower ( $\sim 1.9 \text{ nm}$ ). The crystalline films grown at higher temperatures (1173 K and 8.000 mbar reactor pressure with and without ammonia) were found to have a similar morphology with pyramidal features, but with a higher rms roughness of about 15–30 nm. As verified by AFM measurements, the bare  $\text{Al}_2\text{O}_3$  substrate had a surface roughness of 0.2 nm. The surface morphology of a GaN film grown from BAZIGA, under 8.000 mbar reactor pressure, with a vaporizer temperature of 363 K, without using ammonia, at 1173 K, on *c*-plane  $\text{Al}_2\text{O}_3$ , was analyzed using SEM. It was found that the film was porous and not continuous, with the evolution of some irregularly shaped crystallites

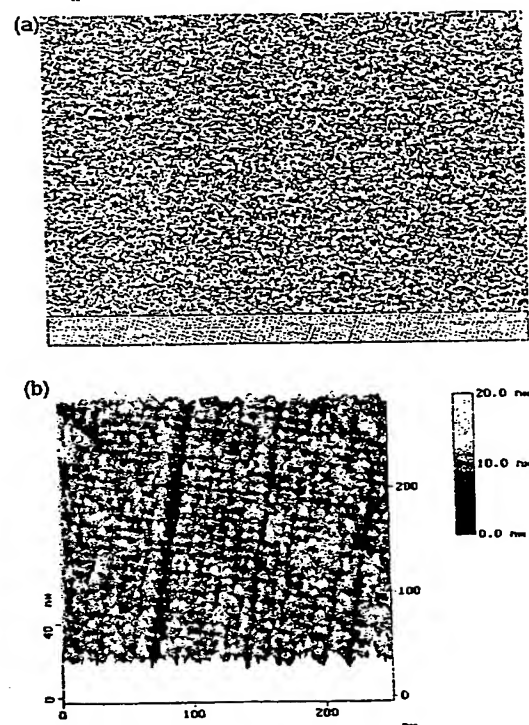


Fig. 8. a) AFM image of a GaN film grown with ammonia (20 sccm) at 873 K. b) SEM analysis of a GaN film grown on *c*-plane  $\text{Al}_2\text{O}_3$  at 1173 K without ammonia, using a GaN buffer layer (grown from BAZIGA at 773 K). All depositions were carried out under 8.000 mbar reactor pressure, at a vaporizer temperature of 363 K, and grown on *c*-plane  $\text{Al}_2\text{O}_3$  substrates.

( $\approx 0.35 \mu\text{m}$ ). On the other hand, the amorphous films grown at low temperature (873 K), under 8.000 mbar reactor pressure, with a vaporizer temperature of 363 K, revealed a dense microstructure with no porosity and a surface roughness of 2.2 nm (as verified by AFM studies). Nucleation is generally believed to be the most critical step for obtaining high-quality GaN layers. The typical growth procedure of GaN from separate sources takes advantage of a thin nucleation layer (buffer layer) of GaN grown at low temperatures (773–873 K), following a tempering step, to induce solid-state epitaxy. Such pre-treatment allows the growth of dense and smooth GaN films at high temperatures. Following this strategy, we aimed to use low-temperature GaN deposition using BAZIGA (773 K, under 8.000 mbar reactor pressure, vaporizer temperature of 363 K) to obtain a buffer layer of this kind. As expected, a subsequent high-temperature growth step (1173 K, under 8.000 mbar reactor pressure, vaporizer temperature of 363 K) with BAZIGA yielded a relatively dense microstructure with greater connectivity, in spite of the grains (Fig. 8b) being larger in size (of the order of  $1 \mu\text{m}$ ). These data illustrate that it is possible to grow GaN films with a well-connected microstructure on a buffer layer, initially grown from BAZIGA on sapphire at low temperatures.



### 2.7. Room-Temperature Photoluminescence

The optical properties of the GaN films grown were characterized by PL measurements, and Figure 9 shows the room-temperature PL spectrum of an epitaxial GaN film

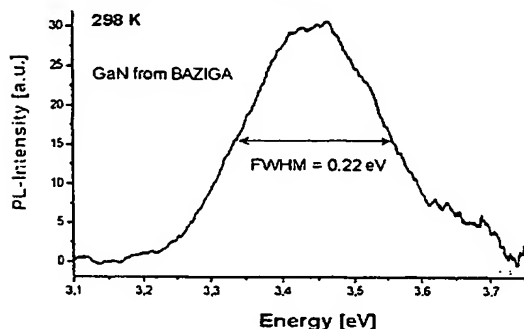


Fig. 9. Room-temperature PL spectrum of a GaN film grown on *c*-plane  $\text{Al}_2\text{O}_3$  at 1123 K using BAZIGA, without ammonia, under 1.000 mbar reactor pressure, with a vaporizer temperature of 363 K.

(grown at 1173 K, under 1.000 mbar reactor pressure, with a vaporizer temperature of 363 K, using BAZIGA without ammonia) exhibiting the correct near band edge luminescence at 3.45 eV (FWHM = 0.22 eV). Our previously reported PL data on GaN films showed only the low energy defect luminescence, not the band edge luminescence.<sup>[25]</sup> These films were grown in a simple hot-wall system in vacuum, without nitridated sapphire or the aid of GaN buffer layers, using a batch of relatively impure BAZIGA (melting point of  $-28^\circ\text{C}$ , as compared to  $35^\circ\text{C}$  for the BAZIGA used for the experiments described in this paper). To the best of our knowledge, there is no other report in the literature on a GaN material grown with any SMP in the absence of additional N sources (e.g., ammonia) giving reference to PL data of the GaN film. However, further optimization of the growth conditions is needed to match the very narrow FWHM of PL (0.09 eV) at room temperature for GaN light-emitting diodes (LEDs) that has been reported for the conventional process using  $(\text{CH}_3)_3\text{Ga}$  and  $\text{NH}_3$ .<sup>[32]</sup>

### 3. Conclusions

It has been demonstrated that, by using the single-molecule precursor BAZIGA, it is possible to grow GaN materials of a structural quality reasonably close to that of the materials grown by the standard process, and exhibiting the characteristic band edge PL at 3.45 eV. This result is surprising, since the derived optimum growth conditions are close to, or even above, the onset of GaN decomposition (at about 1123 K), and no additional N-source (i.e., ammonia) was used to overcome N-deficient growth. In summary, we have achieved low-temperature growth of epitaxial GaN without any additional nitrogen source, using a single-source precursor. The results indicate that single-source precursors such as BAZIGA have serious potential for

growing the nitrides at lower substrate temperatures in stoichiometric ratio, and eliminating the need for large amounts of ammonia, thus leading to a more effective and economical deposition process. Further optimization of the growth conditions and reactor geometry may lead to GaN films of higher quality comparable to those obtained from conventional precursors in an MOVPE process for GaN.

### 4. Experimental

**Precursor Synthesis and Characterization:** The synthesis of BAZIGA for this study was a modified version of that reported in the literature [23,27]. The improved synthetic procedure yielded colorless, needle-like, single crystals below room temperature upon repeated distillation at 423 K under reduced pressure ( $10^{-3}$  mbar). The synthesis was scaled up to larger batches ( $\approx 25$  g), based on the requirements of CVD experiments. Precursor identification and characterization were achieved by a number of different techniques such as IR, NMR, MS, elemental analysis, and atomic absorption spectroscopy (AAS), the details of which are described elsewhere [27]. The thermal analysis (TG/DTA) of BAZIGA was performed using a Seiko TG/DTA 6300S11 instrument in an argon atmosphere ( $100 \text{ mL min}^{-1}$ ) under ambient pressure. The furnace was heated to 773 K at a heating rate of  $5 \text{ K min}^{-1}$ . About 10 mg of the sample was generally used for the analysis. The vapor pressure of the compound was determined using a vapor pressure balance VP433, Netzsch Instruments. Condensation and impulse methods were employed to determine the vapor pressure using about 0.2 g of the precursor in a Knudsen cell.

**Film Deposition:** A horizontal, low-pressure, cold-wall CVD reactor (a schematic is shown in Fig. 2) was fabricated for film deposition. It consists of a quartz tube, length about 50 cm, diameter 2.5 cm, at the center of which the substrates are placed on a SiC-coated graphite susceptor. Substrate heating is accomplished by an inductive heating arrangement attached to a radiation pyrometer. The outer wall of the central zone of the quartz tube is cooled by water. Using this set up, temperatures up to 1473 K can be attained. The susceptor can accommodate substrates as large as 1 inch  $\times$  1 inch although, normally, 1 cm  $\times$  1 cm single crystal sapphire *c*-plane  $\text{Al}_2\text{O}_3$  substrates are used for film deposition. The quartz tube is attached to a glass vaporizer by means of O-ring joints, and the vaporizer is placed in an air bath that can be heated to 423 K. At the rear end of the reactor, a glass trap (cooled by liquid nitrogen) is connected to trap the by-products during the CVD reaction. A turbomolecular pump is used to conduct film depositions at low pressure. The pressure of the reactor is regulated using a motor-driven throttle valve, and the mass flow controllers are used to monitor and control the flow of the various gases used for the process. The substrates were degreased in trichloroethylene, etched in a mixture of  $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$  (3:1) at 353 K, and rinsed with water and acetone before being loaded into the reactor. The precursor vaporizer was filled with about 0.5–1.0 g of BAZIGA. The system was evacuated, and the substrates were subjected to a pre-treatment under vacuum at 1323 K for a couple of hours, followed by hydrogen (99.9999 %, 10 sccm) annealing, at the same temperature, for an additional 30 min. Thereafter the temperature was lowered to 1223 K and the substrate nitridated under ammonia flow (99.999 %, 40 sccm) for 30 min. Meanwhile the vaporizer was heated to, and maintained at, 363 K. High-purity nitrogen (99.9999 %, 40 sccm) was used as the carrier gas to transport the precursor vapor to the reaction zone. After nitridation, the temperature of the substrate was set to a desired value, and the vaporizer valve was opened marking the onset of film deposition. Typically the growth lasted for 30–45 min, and after the deposition was completed, the substrates were slowly cooled to room temperature and recovered for analysis. Normally a step on the substrate was created by masking the substrate in order to calculate the growth rate from step height measurements. Film depositions were carried out as a function of substrate temperature, vaporizer temperature, and reactor pressure, with and without ammonia. The deposition temperature was varied in the range 773–1473 K, while the reactor pressure was varied between 0.080 and 100.0 mbar.

**Thin Film Characterization:** The recovered substrates were characterized by a variety of techniques, and film properties were measured. The thickness of the films was measured using AFM, which was also used to analyze the surface roughness of the nitridated substrates and the GaN films grown. The crystalline properties of the films were investigated in detail by XRD using a D8-Advance Bruker AXS diffractometer. A high-resolution X-ray diffractometer (D8-Discover-Bruker AXS) was employed to perform high-res-

olution, rocking curve analysis of the epitaxial films, reflectometry measurements, and to generate reciprocal space mappings and pole figures. For the rocking curve analysis, a pin hole configuration was used with Cu K $\alpha$  radiation, and a Goebel mirror with a parallel plate collimator combined with 0.1 mm divergence slits were placed in front of the detector. This arrangement permits high intensity with good resolution. The X-ray reciprocal space mappings were obtained by performing the  $\omega$ -scans by inclining the sample continuously along the  $2\theta$  axes, and the pole figures were obtained by rotating the sample along the  $\psi$  axes at different  $\phi$  positions.

Film composition was determined using RBS, XPS, and AES. PL measurements were employed to study the optical properties of the GaN films. SEM analyses were performed using an instrument from LEO, and RBS measurements were conducted using the instrument from DTL (Dynamitron Tandem Laboratory). The XPS measurements were carried out using a Fisons instrument with a CLAM 2 analyzer. The surface morphology was investigated by AFM, using a Nanoscope Multimode III scanning probe microscope (Digital Instruments). Contact-mode imaging was performed applying silicon nitride cantilever-tip assemblies (Digital Instruments) with nominal force constants of 0.06 or 0.12 N m<sup>-1</sup>. The PL was conducted at room temperature using a frequency-tripled Ti-sapphire laser, obtaining an excitation wavelength of 270 nm (pulse duration 200 fs, 50 mW). The laser point density incident on the sample was 100  $\mu$ J cm<sup>-2</sup>.

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